Communication

True Phase Diagrams

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With the use of today's computer softwares, phase diagrams can readily be plotted with a wide choice of variables on the axes. Hillert defined a true phase diagram as a diagram where each point uniquely defines the stable phases. He also showed that not all choices of axis variables give true phase diagrams. In this note we will demonstrate that although the rules stated by Hillert are necessary they are not sufficient to have true phase diagrams.

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Phase diagrams are one of the most important tools to represent information on phase equilibria. A phase diagram is usually 2D and has thermodynamic state variables like temperature and composition on the axes where each point in the diagram represents the stable phases for the particular combination of state variables. With the use of today's computer softwares such diagrams can readily be plotted with a wide choice of variables on the axes allowing the user to choose what is most convenient to address a certain problem. Hillert[1] defined a true phase diagram as a diagram where each point uniquely defines the stable phases. Points representing the same set of stable phases constitute a phase field and the phase diagram then usually shows the boundaries between the different phase fields. In contrast a phase diagram where the phase fields overlap may be thermodynamically correct in principle but is not useful due to the lack of uniqueness. Hillert showed that the choice of state variables must obey certain rules in order to have true phase diagrams. In this note we will demonstrate that although Hillert's rules are necessary they are not sufficient to have true phase diagrams.

As a starting point we show in Figure 1 the classical binary Fe-C metastable phase diagram at atmospheric pressure, *i.e.*, graphite that usually forms very slowly has been removed and cementite Fe_3C forms instead. The metastability is not important in this study; this Fe-C system was simply chosen as a good example to demonstrate the general approach, valid for all systems. Temperature is on the vertical axis and carbon content on the horizontal axis. Inspection of the diagram reveals that this is a true phase diagram. In fact all other binary phase diagrams at a given pressure and plotted with temperature and composition are true phase diagrams. For all the following diagrams no additional phase equilibrium calculation is required because the values of all relevant thermodynamic properties along the phase boundaries are already stored in the memory during this first phase diagram calculation. The calculations can be reproduced using either Thermo-Calc,[2] as done in this study, or Pandat[3] software and the thermodynamic description of the Fe-C system.[4]

In Figure 2 we have exchanged the carbon content with the carbon activity on the horizontal axis. The carbon activity a_C^{ref} is related to the chemical potential of carbon μ_C

$$RT \ln a_C^{ref} = \mu_C - {}^{\circ}\mu_C^{ref} \quad [1]$$

and is given relative to some arbitrarily chosen reference state having chemical potential ${}^{\circ}\mu_C^{ref}$. Here graphite is chosen, ${}^{\circ}\mu_C^{gra} = {}^{\circ}\mu_C^{ref}$, *i.e.*, the carbon activity a_C^{gra} is defined as unity in equilibrium with graphite. As can be seen this is also a true phase diagram although the two-phase fields now collapse to lines and the three-phase fields which were horizontal lines in Figure 1 now are points. In fact Figure 2 has the same topology as a unary phase diagram where usually pressure and temperature are on the axes. This is because the quantities on both axes are thermodynamic potentials. On the other hand one could plot a unary phase diagram with volume as one axis and it would then have the same topology as Figure 1. A phase diagram like Figure 2 is useful when the carbon activity is controlled, *e.g.*, by equilibration with a certain C-bearing atmosphere, and one would like to know what phase forms for certain combinations of temperature and carbon activity. Figure 1 is useful when one rather controls the carbon content by alloying.

Perhaps one would like to know how much heat needs to be added in order to reach a certain constitution for a given carbon content. In that case one should use molar enthalpy, H_m in J(mol-atoms)$^{-1}$, instead of temperature on the vertical axis. This diagram is shown in Figure 3. Here the tie lines connecting points in equilibrium have been added in the two-phase fields. In Figure 3 both the two-phase and three-phase fields are areas. Inspection shows that this is also a true phase diagram and in fact it has the same topology as an isothermal ternary section with composition on the axes.

In the next step we would like to keep molar enthalpy on the vertical axis and rather have activity on the horizontal axis. This is shown in Figure 4. As can be seen this is not a true phase diagram because there are overlapping phase fields. As pointed out by Hillert[1] the choice of state variables must obey certain rules if one wants to have true phase diagrams. Hillert derived permissible sets of variables by considering the combined law written in various forms with different set of

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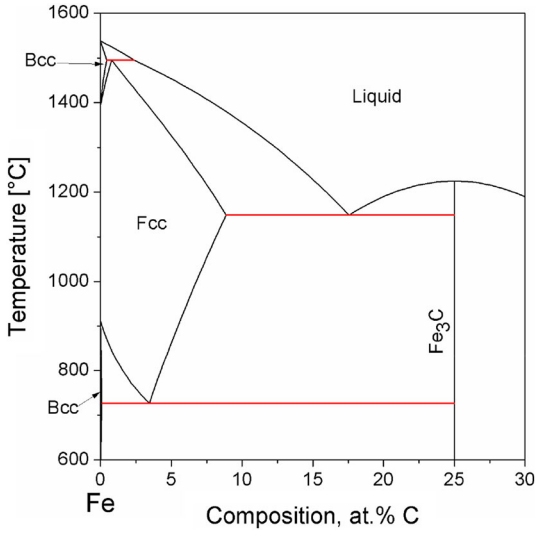


Fig. 1—Metastable Fe-C phase diagram.

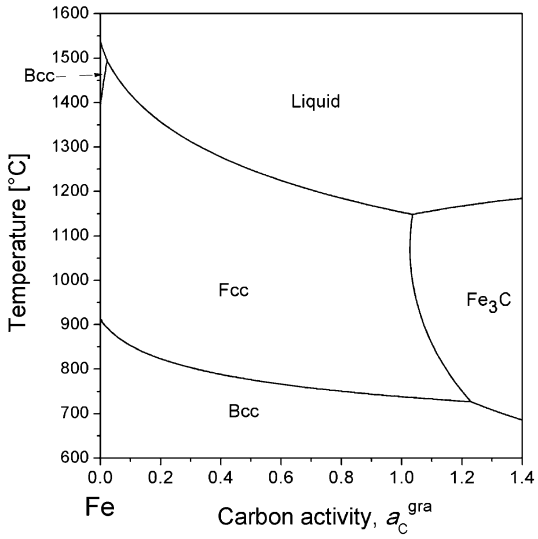


Fig. 2—Metastable Fe-C phase diagram with carbon activity (relative to graphite), a_C^{gra}, on horizontal axis.

conjugated variables. For each set he derived the corresponding Gibbs–Duhem equation and then eliminated one of the potentials to obtain a set of independent conjugated variables. He then showed that in order to ensure a true phase diagram the axis variables had to be chosen within such a set. If variables are chosen from different sets a true phase diagram cannot be ensured. There is a large but finite number of possible sets and he listed several examples in tables.

In the present case the only permissible set that contains both the chemical potential of carbon and the enthalpy is the set where the enthalpy is normalized to the number of moles of Fe, n_{Fe}, rather than to the number of moles of Fe and C as in the normal molar enthalpy. This can be understood more intuitively

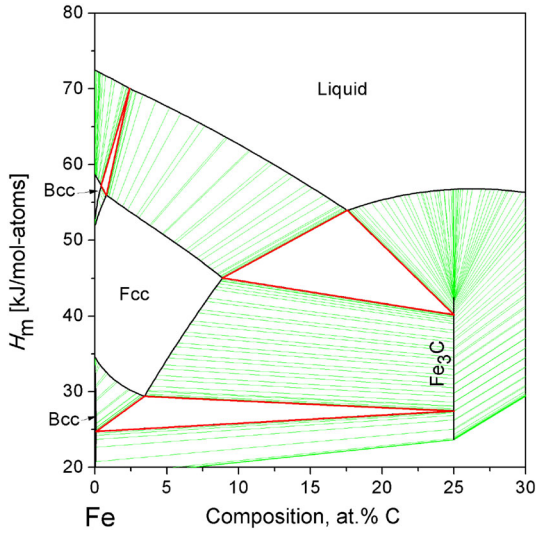


Fig. 3—Metastable Fe-C phase diagram with molar enthalpy, H_m in kJ(mol-atoms)$^{-1}$, on vertical axis and tie-lines added in the two-phase regions. The three three-phase regions are marked by the three triangles.

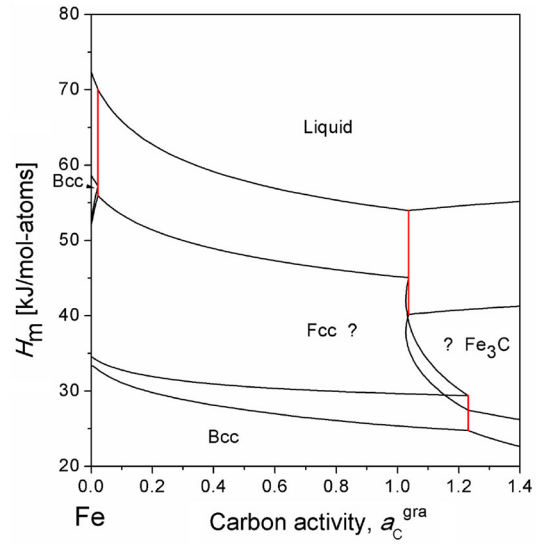
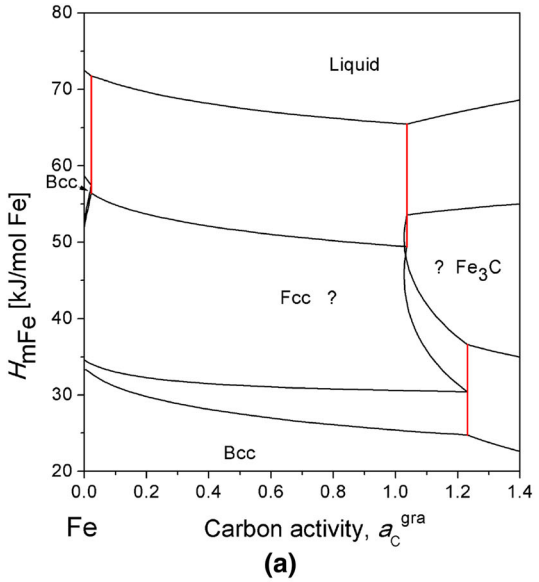


Fig. 4—Metastable Fe-C phase diagram with molar enthalpy, H_m, on vertical axis and carbon activity relative to graphite, a_C^{gra}, on horizontal axis. This is not a true phase diagram as there are various overlapping phase fields.

because it is evident that by controlling the carbon activity the system is now open to a reservoir with defined carbon activity and the carbon content in the system is not fixed. Only the amount of Fe in the system is fixed. The total enthalpy of the system, H, divided by n_{Fe}, can be easily calculated from H_m:

$$H_{mFe} = \frac{H}{n_{Fe}} = \frac{H_m}{1 - x_C} \quad [2]$$



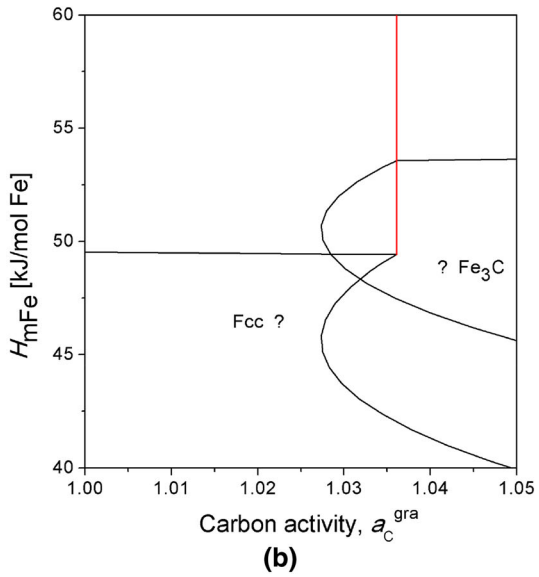


Fig. 5—(*a*) Metastable Fe-C phase diagram with enthalpy per mole of Fe, H_{mFe} in kJ(mol Fe)$^{-1}$, on vertical axis and carbon activity relative to graphite, $a_{\mathrm{C}}^{\mathrm{gra}}$, on horizontal axis. This is not a true phase diagram as there are still overlapping phase fields in the upper right part. (*b*) Enlarged part of (a) showing overlapping phase fields.

Such a plot is shown in Figures 5(a) and (b). Now the three-phase equilibrium in the lower part to the right, Bcc + Fcc + Fe_3C, does not show overlapping phase fields. But a closer examination shows that the three-phase equilibrium in the upper part to the right, Fcc + Fe_3C + Liquid, looks strange. In fact there is some overlapping of phase fields in the upper right part, shown enlarged in Figure 5(b). How is this possible when the rules given by Hillert are obeyed?

In order to understand this behavior we have to realize that energy and entropy have to be given relative some reference. For entropy it is natural to use 0 K (−273 °C) as reference because the third law states that all substances have the same entropy at 0 K (−273 °C)

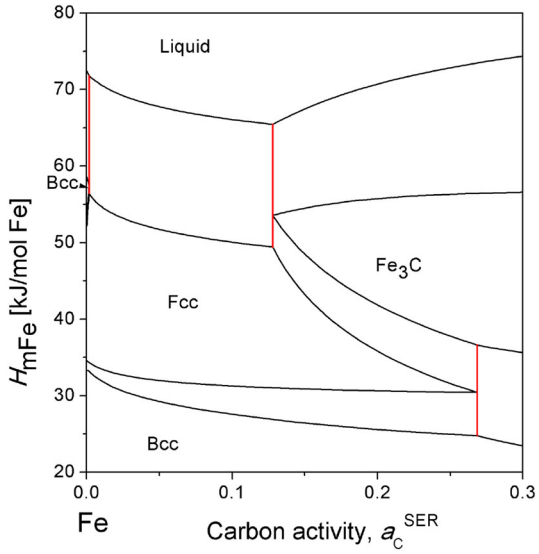


Fig. 6—Metastable Fe-C phase diagram with enthalpy per mole of Fe, H_{mFe}, on vertical axis and carbon activity relative to SER, $a_{\mathrm{C}}^{\mathrm{SER}}$, on horizontal axis. This is a true phase diagram as there are no overlapping phase fields.

and it is custom to set it to zero. For energy there is no such natural reference but it is common to apply the so called Stable Element Reference, SER, *i.e.*, the substance in its stable form at 298.15 K (25 °C) is assigned zero enthalpy. It is important to realize that the choice of reference also affects state functions derived from energy and entropy such as F, G and the chemical potentials. In our diagrams we have so far used different references for carbon in the enthalpy (SER) and the activity (graphite) and of course this may lead to inconsistencies. We may test this using SER as reference for carbon rather than graphite, see Figure 6,

$$RT\ln a_{\mathrm{C}}^{\mathrm{SER}} = \mu_{\mathrm{C}} \qquad [3]$$

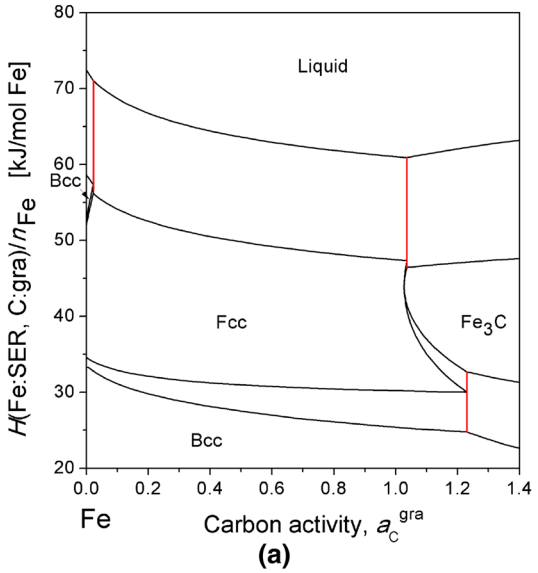
We now find that there are no overlapping phase fields and that this is a true phase diagram. However, for practical purposes it would be more convenient to use graphite as reference for carbon. In order to be consistent we should then use the same reference for carbon in the enthalpy. The total enthalpy of the system that we used so far, H, should be more precisely written as

$$H = H(\mathrm{Fe:SER, C:SER}) \qquad [4]$$

That indicates explicitly the enthalpy reference, being SER for both Fe and C. What we need to use now is H(Fe:SER, C:gra) because only carbon is referred to graphite while Fe still refers to SER. This quantity is calculated by

$$\frac{H(\mathrm{Fe:SER, C:gra})}{n_{\mathrm{Fe}}} = \frac{H_{\mathrm{m}}}{1-x_{\mathrm{C}}} - \frac{x_{\mathrm{C}}}{1-x_{\mathrm{C}}}\left[H_{\mathrm{C}}^{\mathrm{gra}}(T) - H_{\mathrm{C}}^{\mathrm{SER}}\right] \qquad [5]$$

and plotted in Figures 7(a) and (b). We conclude that again we obtain a true phase diagram. In Eq. [5] $H_{\mathrm{C}}^{\mathrm{gra}}(T) - H_{\mathrm{C}}^{\mathrm{SER}}$ is the well-known enthalpy of 1 mol of



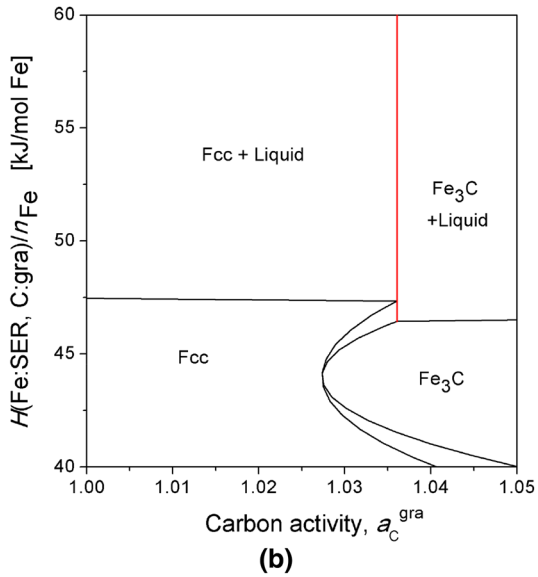


Fig. 7—(*a*) Metastable Fe-C phase diagram with enthalpy per mole of Fe, H(Fe:SER, C:gra)/n_{Fe}, on vertical axis and carbon activity, a_C^{gra}, on horizontal axis. Graphite is used as reference for carbon both in the enthalpy and the activity. This is a true phase diagram as there are no overlapping phase fields. (*b*) Enlarged part of (a) showing no overlapping phase fields where there were overlapping phase fields in Fig. 5(b).

graphite, being zero at 298.15 K (25 °C) and the shift of reference is due to the second term which is absent in Eq. [2].

If one considers Figures 7(a) and (b), which are true phase diagrams, and calculates the quantity H_{mFe} at the phase boundaries for a certain carbon activity, *e.g.*, $a_C^{gra} = 1.03$ (relative graphite) one finds that when a two-phase field is passed in the direction of increasing $H(\text{Fe} : \text{SER}, \text{C} : \text{gra})/n_{Fe}$, see Eq. [5], the quantity H_{mFe} may decrease in some cases. This violates one of the criteria for a true phase diagram stated by Hillert and shows that an equilibrium defined by fixed values of a_C^{gra} and H_{mFe} is not always uniquely defined. If we would like to make an experiment with $a_C^{gra} = 1.03$ and say $H_{mFe} = 45\,\text{kJ/molFe}$ we will find that it can be realized in two different ways. Either by having pure cementite or by having a two-phase mixture Fcc + Cementite with a certain composition. This can actually be seen in Figure 3 although it is plotted with H_m as axes.

We thus conclude that true phase diagrams will be obtained if the Hillert rules are obeyed and if the reference states are chosen consistently.

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